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(54) Title: METHOD FOR IMPROVING THE TASTE OF NUTRITIONAL PROTEIN AND FOODSTUFFS OBTAINED IN THIS WAY

(57) Abstract

The invention provides a method for improving the taste of hydrolysed nutritional protein, by adding an essentially linear polysaccharide to the hydrolysed protein. The polysaccharide is preferably an α-1,4-glucan, derived from starch, and it can be added in an amount of about 0.5-5 weight equivalents with respect to the protein used. The protein thus improved can be lactoprotein or fish, chicken or soya protein, and may be processed into foodstuffs or feedstuffs without the need to separate the polysaccharides.

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Method for improving the taste of nutritional protein and foodstuffs obtained in this way.

The invention relates to a method for improving the taste, and in particular removing the bitterness, of hydrolysed protein.

Bitterness can constitute a problem in virtually every type of foodstuff. In some products, the bitter taste is not always present and this can be related to the degree of ripeness, cultivation conditions and/or environmental factors. On the other hand, in other products the bitter taste can always be present and remain even after dilution of the product with a non-bitter product. For many, if not all, products bitterness is regarded as a sensory defect. The problem is also increased because within a group of people there is a wide variation in the degree to which bitterness is experienced. Some people are already able to detect bitterness in extremely low concentrations, whereas others are able to do so only at very high concentrations. Bitterness is also frequently accompanied by a long-lasting aftertaste.

Protein products constitute an important group of foodstuffs in which the problem of bitterness can arise. In particular, hydrolysed proteins, which may or may not have been split by proteolysis, from milk, fish, chicken and soya are troubled by a bitter taste, in particular after prolonged hydrolysis. This hydrolysis is frequently desirable in order to improve the solubility and/or digestibility. Many amino acids which contribute to the bitterness of hydrolysed protein products are also essential, for example in the human diet.

The bitter taste of, inter alia, milk products is caused in particular by the presence of bitter-tasting amino acids and peptides which are formed as a result of the splitting of (lactose) proteins. This can be the case with matured hard cheese products, with the by-product whey and with milk products which have been treated by the UHT (ultra high temperature) process.

In addition, this problem arises in a very pronounced degree during the hydrolysis of soya proteins. Hydrolysis is necessary for the use of soya proteins in order to improve functional characteristics of the protein and also to increase the solubility. The bitterness of soya protein is the result of the liberation of bitter peptides of differing molecular weights. The intensity of the bitterness is not related to the molecular weight but rather to the amino acids which occupy the C-terminal position and the amino acid composition. This also applies for

the abovementioned cases. The majority of the investigated peptides from hydrolysed soya products contain at least 50% of the relatively hydrophobic amino acids phenylalanine, valine, leucine and isoleucine. A general rule is that the intensity of the bitter taste is correlated to the degree of hydrophobicity and also that in bitter-tasting aqueous solutions there is an inverse relationship to the surface tension.

A number of methods are known for removing the bitter constituents from hydrolysed protein products, in particular those of soya proteins:

1. Separation using solvents
2. Precipitation by, inter alia, cyclodextrins
3. Hydrophobic column chromatography
4. Membrane filtration
5. Microorganisms.

Re 1 An azeotrope of water and sec.-butanol can be used to remove bitter constituents from soya. About 5 to 10% of the total hydrolysed product must be removed for complete removal of the bitterness. The disadvantage is that the use of solvents, in particular alcohols, can be expensive on an industrial scale. Moreover, water in mixtures with organic solvents reduces the solubility of the soya protein, with the consequence that the functionality in nutritional products is impeded (see D.H. Honig c.s., J. Food Sci. 41, 642-646 (1976); G. Lalasidis and L.B. Sjöberg, J. Agric. Food Chem. 26, 742-749 (1978)).

Re 2 Cyclodextrins can be used to remove bitter-tasting proteins from soya. In a batch process up to 30% by weight of cyclodextrins relative to soya (solid) is added for this purpose. In this case, however, according to Japanese Patent Application JP-A-51/184052 (1976) (JP-B-83/43062), only lipid oxidation products and possibly phenolic acids and isoflavones are removed. According to this publication, the use of cyclodextrins for the removal of bitterness caused by protein hydrolysis is, however, precluded. In JP-A-57/18948 (1982) and JP-A-58/175447 (1983) (JP-B-83/50705 and JP-B-90/23150) describe the use of citric acid to hydrolyse the protein at low pH with the aid of acid protease (24 h), followed by neutralisation with calcium hydroxide. The addition of calcium hydroxide gives rise to a precipitate which is removed by centrifuging. A product is formed which is full of taste and is free from bitterness. However, precisely the presence of this taste can be an obstacle to use in certain foodstuffs applications.

Re 3 Bitter and non-bitter peptides can be separated on the basis of their hydrophobic and hydrophilic properties by means of hydrophobic chromatography (G. Lalasidis and L.B. Sjöberg, J. Agric. Food Chem. 26, 742-749 (1978): J.F. Roland c.s. J. Food Sci. 43, 1491-1493 (1978)). Disadvantages are the high costs of the column material and the long process time.

Re 4 Membrane filtration separates molecules on the basis of size. It is possible to remove the bitterness from soya using this technique because the bitter peptide components are often much smaller than the non-bitter macromolecules. Ultrafiltration constitutes and effective process of broad applicability for the removal of flavours from soya. Denaturing of protein is minimal. Many types of membranes and reactors already exist. The service life and durability of the membranes are important points, because the membranes have to withstand numerous cleaning and use cycles (see O. de Rham c.s., J. Food Sci. 43, 642-643 (1978); J.P. Roozen and W. Pilnik, Enzyme Microb. Technol. 1, 122-124 (1979); W.D. Deeslie and M. Cheryan, J. Food Sci., 46, 1035-1042 (1981)).

Re 5 The use of microorganisms to remove the bitterness from soya is still in the early stages of development. US Patent 4,315,946 and J.T. Johansen c.s., C.R. Trav. Lab. Carlsberg, 36, 365-384 (1968) describe microorganisms which are capable of converting bitter amino acids and peptides to flavourings and are compatible with certain foodstuffs (cheese). Special starter cultures having a reduced proteolytic power are used to monitor and to prevent the occurrence of bitterness in cheese and the conditions are adapted during the treatment. Hygiene is an important factor when solving problems with milk products prepared by the UHT process. The disadvantages of the use of microorganisms are discussed by M.L. Speck and D.M. Adams, J. Dairy Sci., 59, 786 (1976).

Netherlands Patent Application 8100280 discloses the addition of carbohydrates which swell substantially in water simultaneously with protein-splitting enzymes to a protein substrate, as a result of which a higher degree of hydrolysis is obtained before the "bitter point" is reached. However, the protein composition is changed by a method of this type.

The aim of the invention is to provide a method with which the unpleasant taste, in particular the bitter taste, of hydrolysed proteins can be reduced effectively without the disadvantages of the methods known for this purpose.

The method according to the invention is characterised in that an essentially linear polysaccharide is added to the hydrolysed protein.

The method according to the invention has the following advantages:

- As the undesired taste-carrying substances can be masked and do not have to be separated off, all protein constituents, and thus also the essential amino acids, remain in the product. If, for example, the mixture is spray-dried in its entirety, no amino acids are removed. This is in contrast to the known methods, according to which the bitter taste components are always removed.
- The method is simple and therefore inexpensive, by virtue of the possibility of spray-drying and, if starch, amylose or amylodextrins are used, of pelleting.
- Hydrophobic and bitter taste-promoting amino acids and peptides are encapsulated. This is in contrast to the known method (JP-A-51/148052), in which cyclodextrins are used and which is alleged not to be suitable for removal of bitterness as a consequence of protein hydrolysis.
- The cost of the polysaccharides to be used can be very much lower than that of the cyclodextrins to be used according to one of the known methods.
- Additional modification of taste, for example by means of citric acid as in the method according to JP-A-58/175447, is prevented.
- The protein hydrolysis per se is not influenced, whereas it is influenced in the method according to NL-A-8100280, and the characteristics of the product are consequently retained.

One explanation for the fact that the bitter taste and any other unpleasant taste is reduced or removed by the method according to the invention can be that the polysaccharides used complex the hydrophobic peptides and/or amino acids causing bitterness and thus prevent the bitter taste from being expressed. Other explanations, however, are in no way excluded.

The term "polysaccharides which are essentially linear" is used to denote polysaccharides which do not have substantial long side chain branching and do not have a cyclic structure. According to this definition, for example, amylopectins and, respectively, cyclodextrins are excluded.

Polysaccharides which can be used are, for example, 1,4-α-glucans (polysaccharides which essentially consist of anhydroglucose units which have glycoside bonds at the α-1-position and the 4-position). These include, for example, starch and fractions and derivatives thereof, such

as amylose and dextrins. Since a spiral structure of the polysaccharide may possibly play a role in masking the bitterness, 1,3-β-glucans for example, for xample microbial polysaccharides such as curdlan and scleroglucan, are also usable. Furthermore, in principle other predominantly linear polysaccharides can also be us d, including those which contain units other than glucose.

According to the invention, α-1,4-glucans are preferred, in particular those which have a chain length (degree of polymerisation, DP) of at least 8 and particularly preferentially at least 12 anhydroglucose units per molecule. Polysaccharides having very long chains can be used, but the effect is not proportionately greater. Therefore, a chain length of at most about 100 anhydroglucose units per molecule is preferred in practice. Polysaccharides of this type which have been found to be particularly suitable are linear amylodextrins. These can be prepared from starch by gelatinisation followed by 1,6-debranching, for example by an enzymatic route using 1,6-glycosidases. Debranching does not have to be complete in order to achieve a good bitterness-removal action. Suitable 1,6-glycosidases are, for example, pullulanase and isoamylase.

The starch from which the polysaccharides to be used according to the invention can be prepared can in principle be any type of starch. Examples are corn starch including waxy maize, wheat starch and potato starch.

The amount of polysaccharide to be used depends on diverse factors, such as the method followed and the intended aim (further processing of all of the protein material or after separating off bitter constituents), the strength of the bitter taste of the starting protein, the nature of the protein and of the polysaccharide, and the requirements which the product has to meet. In general, 0,1-20 weight equivalents of polysaccharide with respect to the protein are used. Preferably, 0.5-5 weight equivalents and more particularly about 1-3 weight equivalents are used.

Proteins and protein derivatives from which the bitter taste can be removed using the method according to the invention comprise all nutritional proteins and derivatives thereof, in particular hydrolysed proteins, because it is in particular in the case of these proteins that bitterness is a problem. The proteins are, in particular, lactoproteins, soya proteins, chicken proteins and meat proteins or degradation products thereof, such as hydrolysed products and other (oligo)peptides. Proteins which have a high content of hydrophobic amino acids, such as valine, leucine, isoleucine and phenylalanine, are especially suitable.

Application of the method according to the invention does not require any special faciliti s. The polysaccharide can simply b add d to a solution or suspension of the hydrolysed prot in and kept in contact with the protein for some tim . The entire mixture can then be worked up in a suitable way, for example by spray-drying. If desired, any precipitate formed, which contains bitter taste components, can also be separated off. The method can be designed for batchwise or continuous operations.

Examples; General

a. Materials

The dextrins are prepared from starch, by treatment, after gelatinisation of the starch with pullulanase for 20 hours at 55°C. The pullulanase used was Promozyme (NOVO, Danmark) in an amount of 4-10 units (PUN)/g of starch. Peptone III (soya protein) and peptone IV (hydrolysed soya protein) were supplied by Sigma Chemicals. Bitter hydrolysed casein BV18 and bitter hydrolysed casein BV50 were supplied by "Melkindustrie Veghel BV" (a division of DMV-Campina, The Netherlands).

b. Preparation of the starting materials

In all examples the starting materials used were solutions which were prepared as follows. The linear dextrins were dissolved in water at 100°C. It was possible to dissolve the proteins and hydrolysed proteins in water at 50-80°C, except for the hydrolysed protein BV50. Even after prolonged heating at 100°C, a small proportion thereof remained behind as an undissolved, greasy foam. It was possible to remove this by centrifuging. This residue was found to be odourless and tasteless.

c. Working-up techniques

Spray-drying of the suspensions was carried out using a Büchi laboratory spray-dryer. The inlet temperature was 110°C; the outlet temperature was about 70°C. Freeze-drying was carried out in accordance with known techniques. The samples were assessed for taste by a panel of 12 employees, comprising 8 men and 4 women, who had not been informed of the purpose.

Example I

A mixture of 10 grams of linear dextrins (obtained from waxy corn by treatment with 10 pullulanase units per gram of starch) and 2 grams of BV18 in 130 ml of water was prepared. After cooling, a very finely divided precipitate formed. The entire mixtur (including precipitate) was worked up by spray-drying. About 7 grams of white powder were obtained; this powder was assessed by the majority of the panel

(8 members) as not bitter and not having an unpleasant taste. Two members of the panel found the taste not substantially different from that of the starting preparati n BV18. All panel members found the linear dextrins to have a neutral, that is to say not pleasant and not unpleasant, taste. A duplicate experiment gave the same results. It should be mentioned that the residue on the glass walls of the spray-dryer had the same taste as the material collected.

Example II

A bitter hydrolysed casein, but now BV50, was processed in the same way as in Example I. Seven of the 12 panel members recognised the taste of the starting material slightly, but assessed the material obtained as being not unpleasant, this being in contrast to the starting material, which was found to be very unpleasant. In this case also, there were two panel members who noticed only a slight difference and who also assessed the taste of the starting protein BV50 as not extremely unpleasant.

Example III

Soya protein (peptone III) was treated with linear dextrins using the same method as in Example I. The taste, which was not bitter but was unpleasant, was found to be no longer present or barely present by the majority of the panel members.

Example IV

Hydrolysed soya protein (peptone IV) was treated using the method described in Example I. The material obtained was found by the majority of the panel to no longer have a bitter taste. A few panel members still vaguely recognised the taste of the starting material.

Example V

After heating in 300 ml of water at 100°C, 10 grams of bitter hydrolysed casein (BV 50) were centrifuged. This gave a loss of about 0.5 gram. 10 grams of linear dextrins (obtained as in Example I), dissolved in 100 ml of water, were added to the centrifuged product. After stirring for one day at room temperature, a precipitate had formed and this was removed by centrifuging. The clear, pale yellow solution was evaporated by freeze-drying. A very voluminous, pale yellow powder was thus obtained. In contrast to the st. ing material, the taste was assessed as not unpleasant by all panel members. The centrifuged precipitate was resuspended in water and spray-dried. In general, the taste of this material was found to be somewhat oily.

Example VI

Repetition of Example V, but using 16 grams of dextrin. The results wer the same as those of Example V. Thre test persons gave a somewhat more favourable assessment of the taste of this preparation than of that obtained in Example V.

Example VII

Carried out in the same way as Example V, but using 24 grams of dextrin. The results were identical to those of Example V. This preparation also was given a more favourable assessment by three people than the product obtained according to Example V. The majority of panel members found that the product tasted better than the starting materials.

Example VIII

Ten grams of wheat starch were gelatinised in 100 ml of water and then treated with 0.5 ml of pullulanase (10 units PUN per g) at pH = 5. After incubating for 20 hours at 55°C, a warm solution of 2.5 g of peptone IV in 30 ml of water was added. After cooling, a precipitate formed. After standing for one day, the entire mixture was spray-dried at a temperature of 110°C. According to all panel members, the bitter taste was found to be no longer discernible.

Example IX

Ten grams of potato starch were treated in accordance with the method of Example VIII. 2.5 g of hydrolysed protein BV50 were added, after which the whole was cooled and spray-dried. 10 of the 12 panel members found the taste to be pleasant, with a flowery accent.

Example X

Example IX was repeated, but using 40 units of pullulanase per 10 g of starch and adding 10 g of hydrolysed protein BV50. According to ten panel members the taste was acceptable and the bitter taste had disappeared; according to four panel members the product had a slight metallic/aspirin-like taste.

CLAIMS

1. Method for improving the taste of hydrolysed protein, characterised in that an essentially linear polysaccharide is added to the hydrolysed prot in.

2. Method according to Claim 1, wherein the polysaccharide is an α-1,4-glucan.

3. Method according to Claim 1 or 2, wherein the polysaccharide is derived from starch.

4. Method according to Claim 2 or 3, wherein the polysaccharide is an amylodextrin.

5. Method according to one of Claims 1-4, wherein the polysaccharide has a chain length of 12-100 anhydro-glucose units.

6. Method according to one of Claims 1-5, wherein the protein is a lactoprotein or fish, chicken or soya protein.

7. Method according to one of Claims 1-6, wherein an amount of polysaccharide of 0.5-5 weight equivalents with respect to the protein is used.

8. Method according to one of Claims 1-7, wherein the mixture obtained is further processed in its entirety.

9. Method according to Claim 8, wherein the mixture obtained is spray-dried.

10. Method according to one of Claims 1-7, wherein the mixture obtained is further processed after separating off a precipitated fraction.

11. Foodstuff for humans or animals, obtained using the method according to one of Claims 1-10.

# INTERNATIONAL SEARCH REPOR

International Application No PCT/NL 91/00180

## I. CLASSIFICATI N OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A23L1/305; A23L1/09

## II. FIELDS SEARCHED

Minimum Documentation Searched[7]

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| Int.Cl. 5 | A23L ; A23J ; A23C |

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## III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

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## IV. CERTIFICATION

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| 25 NOVEMBER 1991 | 06. 12. 91 |
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. NL 9100180 SA 51799

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 25/11/91
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